2019-01-01

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Turner, Andrew

10.1016/j.marpolbul.2018.11.013
Marine Pollution Bulletin
Elsevier

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https://doi.org/10.1016/j.marpolbul.2018.11.013
Accepted 8th November 2018
Embargoed until 8th November 2020

Abstract

Ceramic fragments and fractionated (< 2 mm) sediment have been sampled from two beaches in southwest England, along with sediment from a control beach where ceramic waste was lacking. Analysis of the glazed ceramic surfaces by X-ray fluorescence (XRF) spectrometry returned concentrations of Pb up to 729,000 mg kg^{-1}, while XRF analysis of sediment samples revealed high but heterogeneous concentrations of Pb at the two sites impacted by ceramic waste (median = 292 and 737 mg kg^{-1}) compared with the control beach (median ~ 20 mg kg^{-1}). These observations are attributed to the disposal of contemporary and historical ceramic products, and the subsequent attrition of material and contamination of local sediment. Extraction of a milled ceramic composite (Pb = 2780 mg kg^{-1}) by 1M HCl, revealed a high (34%) environmental mobility and availability of Pb; extraction in a solution of protein, however, suggested a low (0.1%) bioaccessibility to sediment-ingesting invertebrates.

Keywords:

Ceramic fragments; glaze; lead; sediments; contamination

1. Introduction

Heavy metals enter rivers, estuaries and coastal waters through natural erosion in the catchment and from a variety of anthropogenic sources, including municipal and industrial waste, stormwater, metal mining and processing, boating and shipping activities and agriculture (Cave et al., 2005; Pan and Wang, 2012). Sediment is the principal receptacle of metals in these environments, mainly because its high surface area and chemical reactivity allow charged species to readily undergo exchange reactions, adsorption and co-precipitation at the particle surface (Turner and Millward, 2002). Metals may also be present in sediment when associated with discrete, contaminated particulates, like fly ash, paint fragments, tyre-wear particles and microplastics (Pratt and Lottermoser, 2007; Massos and Turner, 2017) which, in some instances, make a significant contribution to overall metal loading. For example, tyre wear particles enriched in Zn, which serves as an activator or accelerator for the rubber vulcanization process, may contribute up to 10% of the sedimentary reservoir in the vicinity of major highways (Voparil et al., 2004), while antifouling paint fragments containing high levels of Cu as a biocide make considerable contributions to the sediment loading in the vicinity of boat repair facilities (Singh and Turner, 2009).

While measuring heavy metals in intertidal sediments from the Tamar estuary, southwest England, using a portable X-ray fluorescence (XRF) spectrometer (Turner and Taylor, 2018), we noted elevated concentrations of Pb at various locations towards the estuary mouth. At one site, concentrations of Pb, but not other metals, were an order of magnitude higher than concentrations in the upper catchment that is impacted heavily by historic mining activities. Sediments at this site were coarse (sand-gravel-pebble) compared with the fine silts of the upper catchment but were characterised by an abundance of visible fragments of ceramic debris that were usually off-white or brown but occasionally brightly-coloured. Subsequent inspection of other beaches in the region revealed that ceramic debris was

commonly present where sediment was relatively coarse, especially towards the high water line. Since lead oxide was (and, in some cases, still is) employed as a flux in the glazing of ceramics (Beldì et al., 2016), it is hypothesized that the presence and attrition of such material may act as a significant source of local Pb contamination.

In this study, sediments and glazed ceramics have been collected from two beaches in the Plymouth Sound region of southwest England and analysed directly and non-destructively for Pb using XRF; an additional beach with little ceramic waste evident was sampled for sediment as a control. In order to evaluate the mobility and environmental significance of Pb from this source, a composite of glazed ceramics was prepared by milling and subjected to XRF analysis and to different chemical treatments, with extracts analysed by conventional inductively coupled plasma techniques.

2. Materials and methods

2.1. Study sites

Plymouth Sound, south west England is an open, macrotidal bay facing the English Channel whose inner waters are up to 40 m deep and are sheltered by a 1600 m breakwater. The coastline is steeply sloping and rocky, with numerous small coves and beaches. The Tamar and Plym estuaries enter the Sound from the north west and north east, respectively, and supply the majority of freshwater to the system. The inner Sound and lower estuaries are urbanised and support a number of maritime, shipping, naval and fishing industries as well as various water sports.

2.2. Sampling

Samples were collected during March and September of 2017 from three sand-gravel-pebble beaches around the coastal zone of Plymouth and at the locations shown in Figure 1; specifically, at Oreston on the lower Plym estuary, Saltash on the lower Tamar estuary, and Firestone Bay in Plymouth Sound. Previous visits to a number of sites and counting with 0.5 m^2 quadrats had revealed that ceramic fragments were most abundant at the former two locations, especially in the upper reaches of the intertidal zone, while the latter location was relatively free of such material.

Three surficial (< 1 cm) intertidal sediment samples of about 200 g were collected using a plastic spatula at three sites from each location that were approximately 20 m apart. Samples were returned to the laboratory in resealable polyethylene bags where they were oven-dried in open crucibles at 40 ^oC overnight. Dried samples were then sieved through a 2 mm nylon mesh and the fine fraction transferred to new polyethylene bags. Fragments of ceramics that were clearly visible to the naked eye were collected manually from a 1 m^2 quadrat centred on the sediment sample sites and counted into a series of polyethylene bags. In the laboratory, ceramics were cleaned with a nylon brush under running water and dried as above before being stored in air-tight polyethylene boxes.

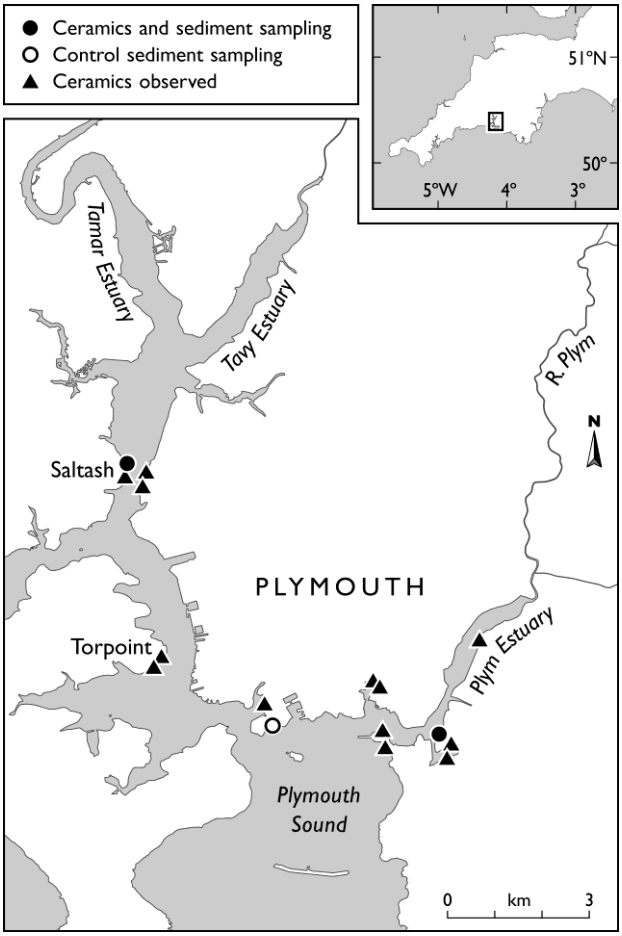


Figure 1: Locations for sampling and where ceramic waste was observed in the Plymouth Sound region of southwest England.

2.3. Sediment analysis

Sediments were analysed directly in their bags and at six different positions through the face of each polyethylene sample bag using a Niton XL3t 950 He GOLDD+ portable XRF housed in a 4000 cm^3 laboratory accessory stand. Measurements for Pb and a suite of other metals whose fluorescent energies were not significantly attenuated by polyethylene (Bi, Cu, Rb, Sb, Sn, Zn) were conducted in a 'mining' mode and with a beam width of 8 mm (equivalent to a measurement area of 50 mm^2) for a total time of 60 s, comprising successive counting periods of 30 s at 50 kV/40 μA (main filter), 15 s at 20 kV/100 μA (low filter) and 15 s at 50 kV/40 μA (high filter). Spectra arising from sample counting were quantified by

fundamental parameter coefficients to yield metal concentrations in mg kg^{-1} and with a measurement counting error of 2σ (95% confidence).

The detection limit for Pb in sediment, based on errors arising from samples returning the lowest concentrations, was around 9 mg kg^{-1}. Multiple analyses of a reference sediment (GBW07318) that had been packed into a polyethylene XRF sample cup (Chemplex series 1400, 21-mm internal diameter) and collar-sealed with 3.6 μm SpectraCertified Mylar polyester film returned concentrations of Pb, Cu and Zn that were within 15 % of certified values (66 ± 6, 66 ± 7 and 165 ± 15 mg kg^{-1}, respectively).

2.4. Ceramic analysis

Selected ceramic samples were analysed by XRF in a 'plastics' mode and a 'lead paint' mode. In the plastics mode, a thickness correction of 0.05 mm was applied that accounted for the film-like characteristics of the glaze. The central area of the glazed surface was measured (and on both internal and external surfaces where possible) for Pb with a beam width of 8 mm and for a total time of 60 s, comprising successive counting periods of 40 s with the main filter and 20 s with the low filter. Concentrations were returned by fundamental parameters in mg kg^{-1} with a detection limit, as defined above, of about 6 mg kg^{-1}. Where the surface was patterned or multi-coloured, different areas were probed by moving the sample with respect to the detector window, a process aided by live imagery generated by the CCD camera adjacent to the x-ray source. Samples of different colour, condition and Pb concentration were also analysed by XRF in a lead paint mode. Here, the instrument was operated at 8 mm and for a counting period of 30 s at 50 kV and 40 μA, and returned concentrations of Pb through fundamental parameters in mg cm^{-2}. Concentrations of Pb determined in six standard reference paint films (SRM 2570 to 2575; National Institute of Standards & Technology) were within 15% of corresponding certified values.

153

154 *2.5. Ceramic composite*

155 A fine, working composite sample of ceramics, representing aged (eroded and abraded)
156 material, was prepared from various fragments of different visual and chemical
157 characteristics. Thus, six fragments from Oreston and six from Saltash were crushed into a
158 powder in a tungsten bowl at 700 rpm for 30 s and 1400 rpm for 20 s using a Retsch RS100
159 puck mill. The powder was transferred into two separate resealable polyethylene bags under
160 a dust extractor, with one bag analysed directly by XRF in its mining mode as above and
161 material in the second bag used in the extraction tests described below.

162

163 *2.6. Extraction tests*

164 The powdered composite was subject to extraction in cold 1 M HCl (Fisher Scientific Trace
165 analysis grade) and 5 g L^{-1} bovine serum albumin (BSA; >96% fraction V, Sigma Aldrich)
166 The former extract is designed as a simple means of evaluating the general mobility or
167 bioavailability of heavy metals and is often used in the first tier of sediment quality
168 assessment (McCready et al., 2003), while the latter extract provides a more specific
169 estimation of metal bioaccessibility to deposit-feeding invertebrates (Kalman and Turner,
170 2007). Thus, three 1 g portions of the composite were weighed into individual 100 ml acid-
171 cleaned Pyrex beakers and 50 ml of 1 M HCl added. The contents, plus three beakers
172 containing acid and no solids, were left at room temperature with occasional agitation for a
173 period of 6 h before being filtered through Whatman 0.45 μm filters into individual 60 ml
174 polypropylene centrifuge tubes. This process, including corresponding controls, was
175 repeated using BSA solution in place of HCl.

176

177 *2.7. Extract analyses*

Concentrations of Pb in the HCl-extracts of the milled composite were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Thermo Scientific iCAP 7400 analyser with a MiraMist PEEK nebuliser and cyclonic spray chamber. The instrument was calibrated using four matrix-matched standards in the range 0.2 to 20 mg L^{-1} and a matrix-matched blank. Instrument RF power was set at 1.2 KW, coolant, auxiliary and nebuliser flows were 12, 0.5 and 0.5 L Ar min^{-1}, respectively, and replicate (n = 3) read time was 2 s. Lead concentrations in the BSA-extracts were determined by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo Scientific iCAP RQ analyser with a Glass Expansion micromist nebuliser and cyclonic spray chamber. The instrument was calibrated with a blank and three matrix-matched standards in the range 10 to 100 μg L^{-1}, and RF power was set at 1.5 KW with coolant, nebuliser and auxiliary flows of 1.4, 1.07 and 0.8 L Ar min^{-1} and a replicate (n = 3) read time of 10 ms.

3. Results

3.1. Characteristics of the ceramic samples

Ceramic fragments were abundant amongst the sand-gravel-pebbles of the upper intertidal zones of Oreston and Saltash, with up to several hundred pieces per m^2 visible at the surface where counting had been performed. Fragments were evident at many other locations in the region (Figure 1), with abundance greater in more sheltered embayments than on beaches facing directly on to Plymouth Sound. In total, 48 ceramic samples were analysed from Oreston and 24 fragments were analysed from Saltash, with a selection of samples illustrated in Figure 2. Samples were an heterogeneous assortment of rounded or angular fragments of earthenware, stoneware and porcelain of different sizes, colours and degrees of aging.

Figure 2: A selection of ceramic fragments retrieved from Oreston and Saltash and presented on cm-scaled paper.

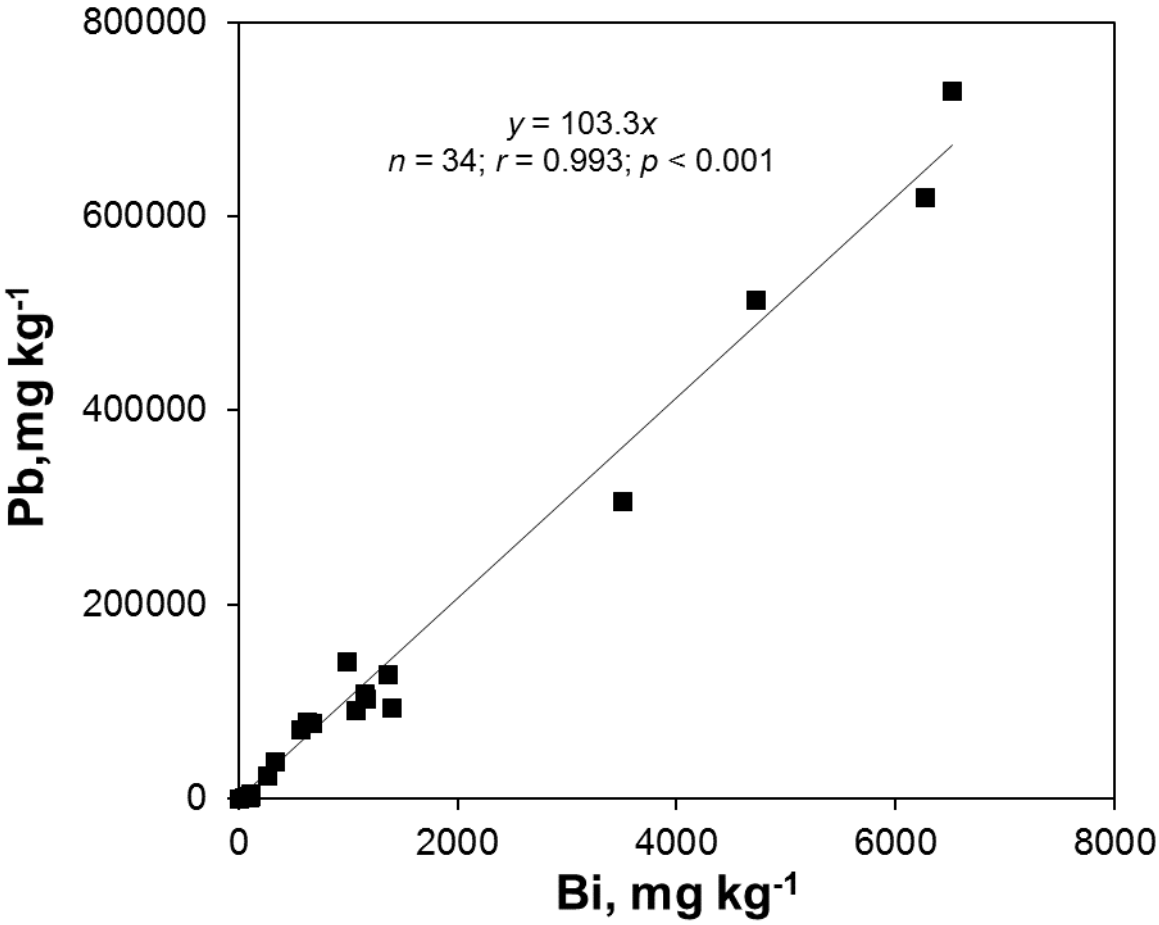
The primary length of most fragments ranged from about 2 to 5 cm, with thicknesses usually around 3-6 mm but that exceeded 1 cm in isolated cases and masses that varied between about 2 and 20 g. Most samples exhibited an inherent curvature and glazing on both surfaces, with many fragments having a distinctive lip or base area and a few fragments characterised by a ribbed or ridged surface; other samples, however, were flat and often unglazed on one side. The décor below glazed surfaces was most commonly white to off-white or brown-beige, with blue-green and yellow fragments also present, while the paste of most samples was off-white or brown. A few samples were decorated in different colours and lipped areas were occasionally coloured differently to the main, curved surfaces. The glazing of some ceramics appeared to be in relatively good condition but the majority of

samples exhibited various degrees of crazing. Other evidence of aging and erosion was the presence of cracks and pits on the surface, areas where the glazing and décor had been completely dislodged from the underlying ceramic body, and regions of inorganic fouling and algal growth.

3.2. Lead concentrations in the ceramic samples

Concentrations of Pb in the glazed surfaces of the ceramic samples from Oreston and Saltash that had been analysed by XRF are summarised in Table 1. Here, concentrations are based on single measurements performed in the centre of the outer surface. Note that multiple measurements over a reasonably uniform surface returned concentrations with a relative standard deviation of < 20% and that measurements of inner surfaces were often constrained by accessibility or distance to the XRF detector window. Lead was detected in all 24 samples analysed from Saltash and in 45 out of 48 samples analysed from Oreston, with concentrations that were highly variable and that, overall, ranged from < 10 mg kg^{-1} to about 70% by weight. There was no clear relationship between Pb concentration and sample thickness, curvature or décor colour but concentrations below 100 mg kg^{-1} were usually encountered in samples that appeared to be relatively clean, angular and new.

Other heavy metals (and metalloids) that were detected by the XRF in many (but not all) ceramic samples analysed included Bi, Cu, Sb, Sn and Zn and with median concentrations of 451, 62, 563, 1160 and 296 mg kg^{-1}, respectively. While the concentrations of the latter elements exhibited no clear co-association with concentrations of Pb, concentrations of Bi (where detected) and Pb exhibited a striking and highly significant linear relationship that is shown in Figure 3.



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241 Figure 3: Concentrations of Pb versus concentrations of Bi in the ceramic fragments.

242

243 Lead was also measured in selected samples (n = 15) on an areal basis using a lead paint
244 mode and with units of mg cm^{-2} that are consistent with many Pb-based paint assessments
245 and regulations (Clark et al., 2006). The concentrations arising from this approach ranged
246 from 0.03 to 23.1 mg cm^{-2} and were highly correlated with concentrations determined in
247 plastics mode and in mg kg^{-1} (r = 0.989; p < 0.001), with a best-fit linear regression line
248 defining the data of y = 29,900x, or a conversion factor between the two measures of 29.9
249 cm^2 g^{-1}. The lead paint mode also returns a depth index that provides a semi-quantitative
250 evaluation of the depth of the layer of Pb. An average value of 1.5 and no values above 2 for
251 the samples tested confirms that the metal is located at or near the surface of the ceramics.

Table 1: Frequency distribution and summary statistics for Pb concentrations (in mg kg^{-1}) in the glazed surfaces of ceramic samples from Oreston and Saltash.

	$< 10^2$	10^2-10^3	10^3-10^4	10^4-10^5	$>10^5$	mean	median	min	max
Oreston (n = 48)	6	10	5	22	5	45,000	29,300	79.0	402,000
Saltash (n = 24)	4	4	3	6	7	121,000	29,900	9.3	729,000

3.3. Lead concentrations in the ceramic composite and release by HCl and BSA

The concentration of Pb in the ceramic composite prepared by milling 12 individual fragments and determined by XRF in mining mode was 2780 $\pm$ 286 mg kg^{-1} (n = 6). Other heavy metals were detected but at significantly lower concentrations; specifically, concentrations of Bi, Sn and Zn were 36.7 $\pm$ 6.2, 46.5 $\pm$ 11.7 and 477 $\pm$ 62 mg kg^{-1}, respectively, and Cu was undetected. Lead mobilised by 1M HCl and determined by ICP was 953 $\pm$ 91.6 mg kg^{-1}, or 34% of total Pb determined by XRF, while the corresponding values mobilised by 5 g BSA L^{-1} were 2.5 $\pm$ 0.86 mg kg^{-1} and 0.1%.

3.3. Lead concentrations in the sediment samples

Concentrations of Pb in the three fractionated (< 2 mm) sediments taken from each location and measured at six different positions through the face of the polyethylene bag are summarised in Table 2. At the control location (Firestone Bay), mean concentrations are similar among the three samples and, overall, concentrations range from about 11 to 30 mg kg^{-1}. At the locations impacted by ceramic waste, both mean and individual concentrations of Pb are more variable, with concentrations ranging from about 80 to 1400 mg kg^{-1} at Oreston and 310 to 1000 mg kg^{-1} at Saltash. On average, Pb concentrations at these locations are greater than the control location by factors of 20 or more.

In order to account for granular and mineralogical variations among the sediment samples, Pb data were normalised with respect to a geochemical proxy. While Al or Fe are conventionally employed as proxies (Schiff and Weisberg, 1999; Ho et al., 2012), the fluorescent energies of the former are too low to be analysed by portable XRF in air and the region is impacted by high and variable concentrations of the latter through acid mine drainage in the upper Tamar catchment (Mighanetara et al., 2009). Accordingly, Rb was selected as a normaliser because of its propensity to substitute for K in fine-grained clays and its ready determination by XRF (Rae, 1995; Lewis and Turner, 2018). Concentrations of Rb, shown in Table 2, reveal relatively invariant concentrations within the same sample and between samples taken from the same site, suggesting that local variations in Pb concentration are not the result of variations in sediment granulometry but are the result of heterogeneous contamination. Variations in Rb concentration between locations, however, suggest that grain size varies across the region; specifically, higher concentrations at Oreston and Saltash than Firestone suggest a finer distribution of material at the former locations.

Rubidium-normalised Pb concentrations were used to compute mean enrichment factors, EF, for sediments at Oreston and Saltash as follows:

$$EF = ([Pb]/[Rb])/([Pb]_b/[Rb]_b)^{-1}$$

where the denominator represents baseline Rb-normalised Pb concentrations that are derived from mean concentrations of the metals at Firestone Bay. Values of EF exceeding unity, shown in Table 2, confirm that the locations impacted by ceramic waste are contaminated by Pb, with the extent of Pb contamination ranging from about 5.4 for one sediment at Oreston to over 13 for a sample from Saltash.

Table 2: Summary statistics for Pb concentrations and mean concentrations of Rb in the three < 2 mm sediment samples from each location that were analysed at six different positions through the face of the polyethylene bag. EF denotes mean enrichment factors for Pb based on normalisation with respect to Rb.

		Pb				Rb	EF
		mean±1 sd	median	min	max	mean±1 sd	
Firestone Bay	(i)	19.5±8.3	15.1	11.4	30.1	50.3±9.2	
	(ii)	21.0±5.2	22.3	14.5	28.3	47.5±3.3	
	(iii)	20.9±6.3	22.0	11.4	28.3	48.6±6.7	
Oreston	(i)	414±488	292	81.3	1390	180±27.7	5.35
	(ii)	564±256	485	304	987	165±23.8	7.95
	(iii)	501±190	425	307	804	168±11.4	6.93
Saltash	(i)	518±181	461	370	872	146±8.1	8.25
	(ii)	481±119	467	307	660	144±22.8	7.77
	(iii)	751±172	737	570	1010	133+18.7	13.13

4. Discussion

While OSPAR (2010) includes ceramics in their categorisation of marine litter, only a handful of studies appear to have referred to this type of waste while classifying beached materials (Ioakeimidis et al., 2014; Buhl-Mortensen and Buhl-Mortensen, 2016). The results of this study are, therefore, significant in revealing the extent of heterogeneous contamination by ceramic debris that is possible in the intertidal zone. Although quantitative analysis was restricted to two beaches around Plymouth Sound, inspections of other local beaches revealed varying degrees of contamination in many other cases (Figure 1), with accumulations most often observed among gravel-pebble deposits of the upper intertidal zone but also apparent on fine, intertidal mudflats. Clearly, it is likely that other environments of similar (historic) usage and setting are subject to comparable contamination by ceramic debris.

Potential sources of ceramics to the region under study include historic landfill sites and various construction projects and manufacturing industries. However, fragments typical of those sampled would be too large and dense to be transported and redistributed across Plymouth Sound, suggesting that sources are more localised. That ceramic debris was more abundant in the vicinity of informal boating activities (repair, maintenance and renovation) implies material may be partly derived from the disposal and fragmentation of shipboard sanitary equipment and tiles. This practice may also attract the tipping of additional municipal wastes, including crockery and garden ceramics, in the immediate vicinity (Turner and Rees, 2016), with lighter material like plastics, ropes and foams more readily swept away or recognised and collected as litter. More generally, however, it is suspected that material has accumulated in the intertidal zone over extended periods of time (centuries) through the historic use of utilitarian and, later, decorated products for the storage, transportation and trading of a wide range of goods, including food, wine, chemicals and molasses. Because of their natural colours, these fragments blend into the sand-gravel-pebble substrate and have, therefore, evaded collection and disposal as waste.

The majority of the ceramic fragments retrieved in the present study were glazed, with surfaces that were usually characterised by high concentrations of Pb. This observation is consistent with the pervasive use of lead oxide (PbO) as a flux of low melting point, wide firing range and high refractive index. Other oxides that were evident in some of the samples and that co-existed with high concentrations of Pb included those of Sn and Zn. However, the striking correlation of Bi with Pb suggests that bismuth trioxide (Bi_2O_3) has been used extensively as a component of ceramic fluxes in tandem with PbO (and at a mass ratio of Pb:Bi of about 100).

High concentrations of Pb in the glaze affords the potential for heterogeneous contamination of local sediment as the ceramics break down through weathering and abrasion; this is reflected by high (but variable) EF values at Oreston and Saltash for sediments fractionated to < 2 mm. It is unclear how thick the glazed layer of the ceramics is but the Pb concentration of the milled composite of 2800 mg kg^{-1} is assumed to be a representative value for the bulk material (that includes the paste) as a contaminant. Thus, assuming a background sediment concentration of Pb for the region of 20 mg kg^{-1} based on results for the control location and a sediment concentration of 400 mg kg^{-1} representative of sites contaminated by ceramic debris, mass balance requires that, on average, ceramic-derived material contributes about 14% to the total mass of (< 2 mm) sediment in contaminated settings.

The mobility or general availability of Pb in the milled composite of ceramics was evaluated using cold 1M HCl. With respect to estuarine and coastal sediments, this fraction is often assumed to represent metal bound in non-residual fractions and where the majority of anthropogenic metals reside, as well as providing a general proxy for monitoring the bioavailability and biological effects of heavy metals (Riddle et al., 2003; Bettiol et al., 2008). While the percentage of total Pb mobilised from the ceramic composite (around 34%) is lower than that typically mobilised from contaminated sediments (in excess of 80% has been reported; McCready et al., 2003), it is nevertheless significant and indicates that the weathered and eroded glaze of ceramics may be an important source of mobile Pb in coastal sediments impacted by visible debris. In contrast, however, the availability of Pb in the composite to the protein, BSA, is only about 0.1% of its total content and is considerably lower that the percentage mobilised in contaminated sediment (around 10%; Kalman and Turner, 2007). Thus, despite its high mobility under acidic conditions, Pb in ceramic debris

is not predicted to be particularly accessible in non-acidic digestive conditions typical of sediment-feeding invertebrates or under near-neutral aqueous conditions more generally.

5. Conclusions

This study has highlighted the potential significance of glazed surfaces as a source of Pb to estuarine and coastal sediments that are visibly impacted by ceramic wastes. At the sites under investigation, the presence of glazed ceramics that have been eroded to sizes < 2 mm result in increases in Pb concentrations relative to a regional baseline of about an order of magnitude and enrichment factors normalised to Rb of between 5 and 13. Lead arising from glazed ceramic surfaces has a mobility of more than 30% as evaluated by extraction in cold HCl, but is unlikely to be assimilated by deposit-feeding invertebrates because of its poor solubility in a surrogate digestive protein. While the specific findings of the study are localised, it would be reasonable to assume that the broad impacts documented are more generally applicable where ceramic waste is observed.

Acknowledgements

This study was partly funded by a HEIF Plymouth University Marine Institute grant. Dr Andy Fisher and Mr Ben Lowe are thanked for assistance with the preparation and analysis of the ceramic extracts.

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